DIAMOND FILMS

Chemical Vapor Deposition for Oriented and Heteroepitaxial Growth

Koji Kobashi

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Preface

The major purpose of this monograph is to review process technologies for oriented and heteroepitaxial growth of diamond by microwave plasma chemical vapor deposition (CVD). There are many CVD methods to synthesize diamond films using, for instance, hot filament, radio-frequency (rf) plasma, microwave plasma, DC plasma, arc-jet plasma, and combustion flame. Among these, this monograph mainly focuses on microwave plasma CVD. The microwave plasma is an electrode-free discharge so that the contamination of diamond films by electrode materials can be avoided. The microwave plasma is very stable over many days, and a subtle control of the plasma, and hence the properties of synthesized diamond films, is possible. This is particularly important to quantitatively investigate the diamond nucleation and the film morphology in oriented and heteroepitaxial growth. This monograph also includes research results that are related to oriented and heteroepitaxial growth.

Historically, a vapor growth of diamond was first demonstrated by W. G. Eversole, which was followed by an intensive research in B. V. Derjaguin's group in Russia and J. Angus' group in the USA. A revolutionary advancement in diamond CVD occurred in the early 1980s, when B. V. Spitsyn et al. demonstrated a growth of diamond particles by CVD (by the chemical transport method), and N. Setaka and co-workers disclosed three methods to synthesize diamond films: hot filament, rf plasma, and microwave plasma. This triggered intensive R&D in Japan, Europe, US and then all around the world. The progress of diamond film research has been very steady and consistent, and numerous findings have been made during the past two decades.

One of the most remarkable findings in the area of diamond CVD is the growth of azimuthally oriented diamond films with (100) faces aligned in the same direction at the film surfaces by B. Stoner and J. Glass in 1992. Such films are now called highly oriented diamond (HOD) films. A key to make HOD films is to use bias-enhanced nucleation (BEN) discovered by S. Yugo, and thus a number of works have been done on diamond nucleation using BEN. The standard substrates for HOD film synthesis are β-SiC(100) and Si(100). One of the best-coalesced films was successfully synthesized by H. Kawarada, P. Koidl and their co-workers, as well as X. Jiang and his co-workers. In the mid 1990s, it was discovered that (111) and (100)-oriented, spontaneously coalesced diamond films could be synthesized on Pt(111) and Ir(100) by Y. Shintani and A. Sawabe, respectively, showing the possibility of producing single crystal diamond films by CVD. Since the growth rate of diamond films has

been remarkably increased in recent years from the past rate of $\sim 0.2\,\mu m/h$ to $\sim 50\,\mu m/h$, and large CVD reactors of maximum 60–100 kW are commercialized, production of single crystal diamond plates is expected to begin in the not-too-distant future.

Under these circumstances, it would be of significance to review the articles on oriented and heteroepitaxial growth of diamond films by CVD, and particularly summarize the processing conditions for the readers to further develop and elaborate the science and technology of diamond CVD. It is expected that this monograph would be useful for such purposes.

In completing this monograph, I must acknowledge many people. First of all, I wish to thank late V. Chandrasekharan, D. Fabre, M. L. Klein, and R. D. Etters for my education in physics before I became an independent researcher. On diamond CVD, I am particularly indebted to N. Setaka, Y. Sato, and M. Kamo for kindly allowing me to learn diamond CVD in their group. I certainly would like to thank my colleagues in Kobe Steel, Ltd.: K. Nishimura, K. Miyata, T. Tachibana, Y. Yokota, K. Hayashi, and N. Kawakami. I wish to particularly thank T. Tachibana for supplying a number of papers related to heteroepitaxy. I would also like to thank my superiors in the company: T. Horiuchi, Y. Kawate, Y. Kawata, Y. Sugizaki, J. Miyazaki, H. Sato, and S. Suzuki for their consistent support of R&D of diamond films over two decades. A longtime friendship with J. Glass, R. Nemanich, and A. Gicquel was a strong encouragement for me to write this monograph. Finally, I would like to thank my wife Toshiko and my son Akira for creating a calm environment for me to work at home. This monograph would not have been published without the support of the people mentioned above.

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Overview of Oriented Growth

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Chapter 1
Overview of Oriented Growth*

Science and technology of diamond film growth by chemical vapor deposition (CVD) have markedly advanced during the past decade. One of the most notable achievements is the growth of azimuthally oriented diamond particles on β-SiC by Stoner and Glass [1, 2] using Yugo's method of bias enhanced nucleation (BEN) [3], which then led to the growth of (100)-oriented diamond films on Si(100) that were later named as highly oriented diamond (HOD) films [4]. This technique was further elaborated by the groups of Glass, Koidl, Klages, and Kobe Steel [5] amongst others. Most recently, Kawarada et al. [6, 7] were successful in growing perfectly coalesced, (100)-oriented, 300-μm thick HOD films, where there was no grain boundary at the film surface. In the meanwhile, a new method of diamond heteroepitaxy was heuristically found by Shintani [8, 9], i.e. spontaneously coalesced, (111)-oriented diamond films can be grown on (111) surfaces of Pt that have been polished with diamond powder for diamond nucleation. This finding was followed by diamond heteroepitaxy on Ir(100) by Sawabe's group [10] using direct current (DC) plasma CVD, in which (100)-oriented, perfectly coalesced diamond films were grown. This work was reproduced by Morooka's group [11], and Schreck and Stritzker's group [12] using microwave plasma CVD (MPCVD), where the diamond nucleation was done by BEN.

Figures 1.1 (a)–(c) show a polycrystalline diamond film deposited on Si substrate, an HOD film grown on Si(111) surface, and a partially coalesced film on Pt(111) substrate, respectively, all synthesized by MPCVD. Diamond films grown on Ir(100) are so perfectly coalesced that there is no feature in the film surface image by scanning electron microscopy (SEM) (see Figure 12.18 [13]). At the present stage, the coalesced area is the largest for diamond films on Ir(100) [25 mm] followed by those on Pt(111) (~10 mm, see Figure 12.8 [14]), while the crystal facets are the smallest for polycrystalline diamond films (see Figure 1.1 (a)). In the latest technology, however, the edge lengths of crystal facets become extremely large even for polycrystalline diamond films. For instance, they are

*In this monograph, a number of notations, units, and abbreviations will be used, and they are summarized in Appendix A. It contains lists of notations for crystal orientations, process parameters for CVD, analytical techniques, CVD reactors, crystal growth, and carbon materials in addition to a description of standard diamond film characterizations, i.e. Raman spectroscopy and cathodoluminescence (CL). The readers are recommended to just quickly read through Appendix A at this point.